

Potential of Local Clay for the Development of Limestone Calcined Clay Cement in East Java

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Abstract. Limestone Calcined Clay Cement (LC3) offers an innovative and sustainable alternative to traditional binders, utilizing calcined clay and limestone as partial substitutes for Ordinary Portland Cement (OPC) clinker. This study investigated the potential of local clays found in East Java, Indonesia, for LC3 production. Clay samples from three sites in East Java, with pure kaolin as a benchmark, were assessed. A formulation with 50% OPC clinker substitution was employed, integrating limestone powder, calcined clay, and gypsum. The clays underwent drying, grinding, sieving, and calcination at both 700°C and 800°C. For comparison, a sample of local Trass, typically used in Portland Composite Cement, was also evaluated. Compared to OPC, the LC3 samples exhibited reduced workability and a faster initial setting time. However, the LC3 mortar displayed commendable compressive strength, achieving a Strength Activity Index exceeding 75% at 28 days. The calcination temperature influenced the ultimate strength, especially in specimens with a higher kaolin concentration. One of the local clays, sourced from Trenggalek, with a kaolinite content of 49%, achieved a compressive strength of 43 MPa at 28 days. This value closely parallels the strengths of both OPC (49 MPa) and the metakaolin (42 MPa) mixtures.

1 Introduction

The cement industry has significantly contributed to global CO₂ emissions, accounting for approximately 5-7% of the world's CO₂ discharges. This translated to almost 0.9 tons of CO₂ emitted for every ton of cement produced [1,2]. A strategy to promote the production of environmentally friendly concrete was the inclusion of cementitious materials in cement formulations, either as additives or replacements for conventional cement. Supplementary cementitious materials like Fly Ash (FA), Slag Cement/Ground Granulated Blast Furnace Slag (GGBFS), and Silica Fume (SF) were among the commonly incorporated materials in cement mixtures [3]. However, the availability of FA and GGBFS dwindled, and it decreased further due to shifts in the coal and iron sectors. The declining availability, combined with

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the rising costs of FA and GGBFS, made these SCMs less cost-effective. Therefore, alternative solutions became imperative to reduce CO₂ emissions from cement manufacturing. One promising approach was the use of calcined clay and limestone to reduce the clinker content in cement formulations [4–8].

Limestone Calcined Clay Cement (LC3) consists of clinker, limestone, calcined clay, and gypsum. Clays, particularly those enriched with minerals like kaolinite, smectite, and illite, became reactive upon calcination and served as partial replacements for clinker [9,10]. An optimally formulated LC3 mixture allowed a higher rate of clinker substitution without sacrificing strength, incorporating limestone and calcined clay [11,12].

Globally, particularly in Indonesia, deposits of kaolinite-rich clay were plentiful [13]. In the LC3 framework, clays with a kaolinite content below 40% were classified as low-grade. While in Java Island, especially East Java, that wasn't primarily known for extensive kaolinite-rich clay deposits, it was found to have both low and high-grade clays suitable for LC3 production. Both these grades of kaolinite clays showed promise as LC3 ingredients. Studies from countries such as India [14] and the UK [15] highlighted the potential of low-grade kaolinite clay in LC3. Further, research examining the correlation between the kaolinite content of clays and the resultant LC3 showed that LC3-50, with 40% metakaolin, matched the strength of Portland Cement at 7 days and surpassed it on the 28th and 90th days [16]. Although kaolin content had a strong association with LC3 performance, clays with identical kaolin concentrations didn't uniformly produce similar strength LC3. This indicated that the overall composition of a clay, whether low or high grade, played a role in shaping the performance of the resultant LC3 binder.

Transitioning to sustainable alternatives like LC3 not only reduced environmental impacts but also drove economic growth by utilizing local resources and potentially lowering construction expenses. In areas like East Java, where materials such as trass had historically been favored, the introduction of LC3 proposed an intriguing dynamic for comparison. Beyond the clear environmental benefits, leveraging local clays for LC3 fortified local economies, diminished transportation-related emissions, and rendered construction more economical. The objective of this research was to explore the suitability of local clays in East Java for LC3 production. This investigation assessed the composition of these clays and their potential as replacements for traditional cement via LC3 technology, with an emphasis on their availability and performance in LC3 blends.

2 Materials and Methods

2.1 Materials Preparation and Characterization

The study involved several materials selected to make a suitable LC3. We sourced OPC and its clinker from Semen Indonesia Group (SIG) Gresik and pure kaolin from a chemical supplier. The local clays, labeled as A, B, and C, came from different regions of East Java, Indonesia, namely a borehole in East Surabaya, a borehole in West Surabaya, and Sukorejo village, Trenggalek, respectively. All these clays and trass were oven-dried for 24 hours, then milled and sieved passing sieve #200 (74 μm). Limestone powder passing a sieve #2,000 (345 μm) and gypsum powder were procured from local supplier. This research utilized silica sand with a fineness modulus of 2.053 to make mortar specimens.

The local clays and kaolin clay were calcined using a laboratory furnace. For this process, 600 grams of each sample was placed in stainless steel containers before being introduced into the furnace. Two temperatures, 700°C and 800°C, were explored, and each calcination process held the maximum temperature for 90 minutes. Once calcination was completed, the samples were allowed to cool for 2 hours, were then weighed, and stored in airtight

containers. Thermogravimetric analysis (TGA) was conducted on all the clays and trass to analyze their material properties. The kaolinite content in local clays and the kaolin clay was calculated using Equation 1 [10]. This equation allowed us to determine the percentage kaolinite content, factoring in mass loss occurring between temperatures of 400°C-650°C and considering the relative atomic masses of $Al_2(OH)_4Si_2O_5$ (kaolinite) and H_2O (water). Furthermore, X-ray diffraction (XRD) tests were conducted on local clay samples A and C, as well as the kaolin clay that had been calcined at 700°C. The kaolin clay after calcination is named metakaolin (MK).





$$wt\%_{kaolinite} = wt\%_{kaol-OH} \frac{M_{kaolinite}}{2M_{water}} \tag{1}$$

The processed materials are shown in Table 1. The clinker and trass were oven-dried for 24 hours and milled, while for the kaolin clay and local clays were subjected to the 700°C and 800°C calcination process. This temperature differentiation was crucial in understanding the thermal behavior and its impact on the final properties of the mixtures. There were color changes on the clays from the calcination process. The clay C initially already had some brownish color turned to a shade of red, while the clay A and B have darker color initially.

2.2 Mixtures Proportion and Testing

The mixture proportions used in this study are presented in Table 2. For the study, a binder-to-aggregate (sand) ratio of 1:2.7 was chosen with a water-to-binder (w/b) ratio set at 0.5. Eleven mix designs were employed, starting with a 100% OPC (Ordinary Portland Cement) control mixture. To investigate the pure filler effect, a mixture of 50% OPC with limestone powder (LP) was used. The following mixtures introduced different materials that is employed in make the LC3-50 mixture, where the OPC clinker was limited up to 50%, and the rest is replaced by a combination of calcined clay, gypsum, and limestone powder, optimizing both sustainability and performance. Within the scope of this research, trass was employed as a substitute for calcined clay in the ternary blend of LC3. This was primarily to compare the performance of trass and calcined clay when incorporated into LC3 mixtures

Table 1. Preparation of the materials used for the experimental study

Material	Initial Condition	Oven Dry + Milled	Calcined 700°C	Calcined 800°C
Clinker (SIG Gresik)			na	na
Trass (Pasuruan)			na	na

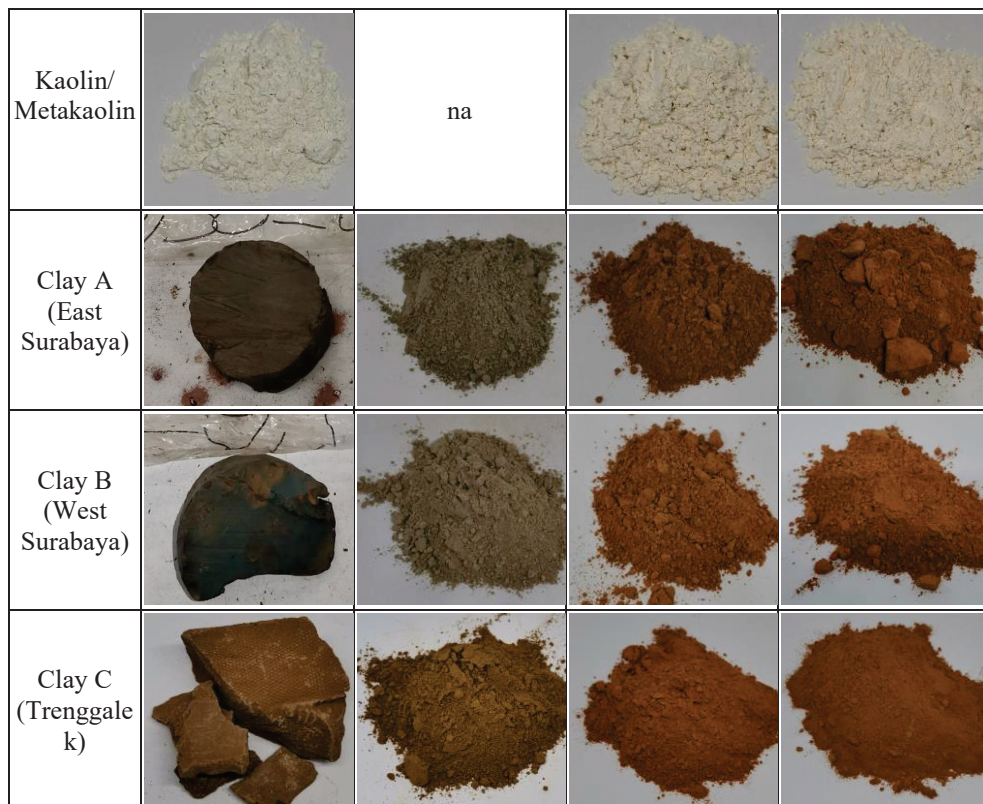


Table 2. Mixture proportion for the mortar for compressive test

No.	Mixture name	Binders							Sand (g)	Water (g)
		OPC (g)	Trass (g)	Metakaoлин (g)	Calcined Clay (g)	Clinker (g)	Limestone powder (g)	Gypsum (g)		
1	OPC 100%	500	0	0	0	0	0	0	1350	250
2	OPC+LP 50%	250	0	0	0	0	250	0	1350	250
3	Clinker+Trass+LP	0	150	0	0	250	75	25	1350	250
4,5	LC3 MK 700/800	0	0	150	0	250	75	25	1350	250
6-11	LC3 Clay (A, B, C) 700/800	0	0	0	150	250	75	25	1350	250

The fresh properties of the mixture were assessed using the Vicat apparatus to determine normal consistency and initial setting time [18,19]. The normal consistency indicated the optimal water amount required for paste workability, while the initial setting time reflected the reaction rate of the mixture. For the hardened mortar, compressive strength was evaluated using 50 mm cube specimens, and flexural strength was determined using prism specimens with dimensions of 40 mm x 40 mm x 160 mm. Samples were submerged in water for curing and were removed only two days before the scheduled tests. Compressive strength

evaluations were conducted on samples at 3, 7, and 28 days, while flexural strength testing was specifically for the 28-day samples.

3 Results and Discussion

3.1 Material Characteristics

The results of the Thermo-gravimetric Analysis (TGA) demonstrate the changes in mass as a function of temperature is shown Figure 1. From the TGA data, it was observed that the kaolin sample showed a significant change in the temperature range of 400-600°C, experiencing the fastest mass decrease at 500°C. For samples of clay A, B, and C, each exhibited a mass reduction in the 0-100°C range, which then plateaued until the calcination temperature, this was due to the drying of the materials. The mass reduction between 400-650°C for each sample was then recorded. Kaolinite content of each material is shown in Figure 1 calculated based on equation 1 by considering the oven dried temperature of 100°C as their initial weight. All samples began to show a leveling off in mass reduction between 500–600°C, indicating that the first calcination had been achieved. Under ideal firing conditions, a temperature of above 600°C should be sufficient for calcination of each sample provided they receive adequate firing time. The TGA results for the trass did not show any significant mass loss showing that it did not undergo calcination.

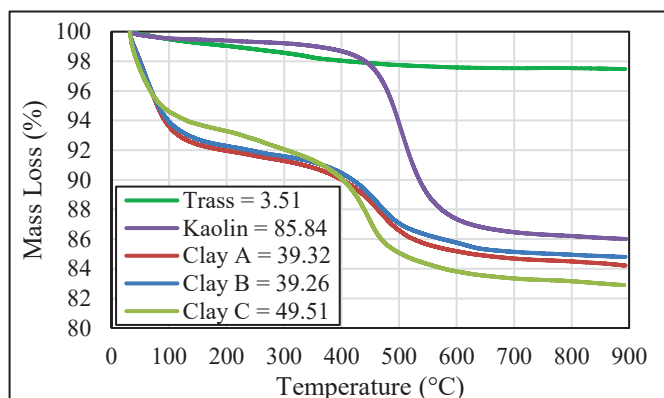


Fig. 1. The mass loss of the sample from the TGA

Figure 2 show the XRD result of the calcined kaolin, clay A, and clay C at 700°C. The calcined kaolin sample exhibited the lowest crystallinity and the highest amorphous content among the three samples, followed by calcined clay C and then calcined clay A, the latter having the least amorphous content and the highest crystallinity. Table 3 also displays the quantitative XRD results of these samples. The residual kaolinite content in the calcined samples was extremely low, indicating that the calcination process conducted at 700°C effectively calcined nearly all the kaolin content within the clay and initiated the dehydroxylation reaction of kaolin into metakaolin. The presence of quartz, which remains inert even post-calcination, has the potential to reduce the reactivity of the clay and the performance of the resultant LC3. The XRD results also revealed that clay A's composition was more diverse, with a higher illite content compared to clay C, which leaned more towards being kaolinitic clay. The varied clay mineral content in clay A might necessitate different treatments compared to kaolinitic clay to achieve optimal performance.

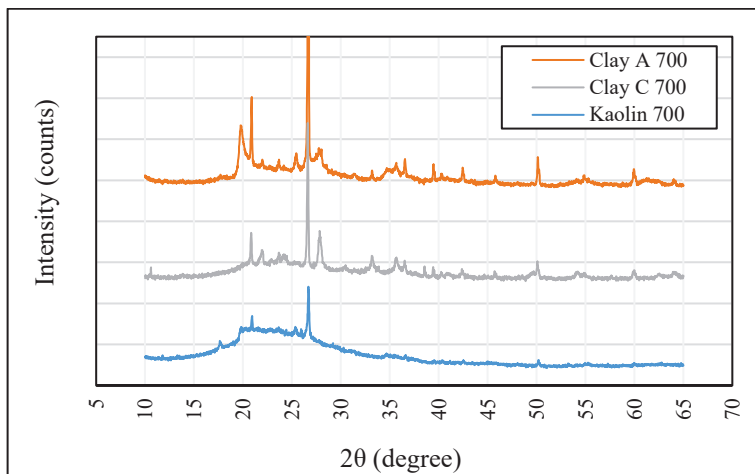


Fig. 2. The result of the XRD analysis for the calcined clay samples

Table 3. Crystal Composition for the Calcined Clay and Kaolin

Crystal name	Content (%)		
	Clay A 700	Clay C 700	Kaolin 700 (MK)
Quartz	20.19	1.25	3.53
Illite	18.5	9.94	1.61
Kaolinite	1.64	0.16	0.01
Amorphous	34.32	57.38	87.08

3.2 Fresh Properties

Tests for normal consistency and initial setting time were conducted on the paste mixture, and the results are presented in Table 4. The workability of the LC3 mixture was found to be lower than that of the OPC mixture. An observed direct correlation was noted between kaolinite content and workability: as the kaolinite content increased, a corresponding increase in the normal consistency values was recorded. For LC3 samples with local clays (A, B, and C), lower values than the control LC3 metakaolin were registered, likely due to their lower kaolin content. This observation aligns with findings by Canbek et al. [17], who determined that an increase in metakaolin content led to a decrease in workability. The water demand in the normal consistency values was found to correspond to the calculated kaolinite content in each clay sample, with the benchmark metakaolin requiring the highest water-to-binder ratio.

Table 4. Result of Normal Consistency and the Initial Setting Time of the Paste Mixture

No.	Mixture name	Normal Consistency	Initial Setting Time (mins)	No.	Mixture name	Normal Consistency	Initial Setting Time (mins)
1	OPC 100%	0.3	145	6	LC3 Clay A 700	0.41	75
2	OPC+LP 50%	0.3	105	7	LC3 Clay A 800	0.41	75
3	Clinker+Trass+LP	0.31	105	8	LC3 Clay B 700	0.4	75
4	LC3 MK 700	0.46	105	9	LC3 Clay B 800	0.4	75
5	LC3 MK 800	0.46	105	10	LC3 Clay C 700	0.43	90
				11	LC3 Clay C 800	0.43	90

Regarding the initial setting time recorded in the Vicat test, a correlation with the normal consistency values was identified. Paste mixtures with higher normal consistency values, and consequently higher w/b ratios, were found to take a longer time to reach their initial setting times. Among control mixtures, those incorporating limestone were observed to set faster than the OPC-only mixture, likely due to the limestone's water absorption capability, which expedited the setting process. In this study, all clays and kaolins used in the LC3 mixtures were calcined at two distinct temperatures: 700°C and 800°C. No variations in normal consistency or initial setting time for identical clay samples were identified. Any discrepancies in the consistency and setting time of the LC3 mixtures were attributed to the clay type variations, specifically the kaolin content within each clay.

3.3 Development of Compressive Strengths

The compressive strength test results for samples at ages 3, 7, and 28 days are depicted in Figure 3. Both LC3 mixtures using metakaolin and local clay demonstrated promising initial strengths at 3 and 7 days, rivaling the strength of OPC at similar ages. Notably, Clay C samples displayed robust early strength; by day 3, their strength nearly equaled the OPC 100% on day 7. Even with reduced kaolinite content (49% compared to 85%), the strength of the LC3 clay C samples was comparable to the metakaolin. Clays A and B also achieved respectable strengths, even with only half the kaolin content of the LC3 metakaolin sample

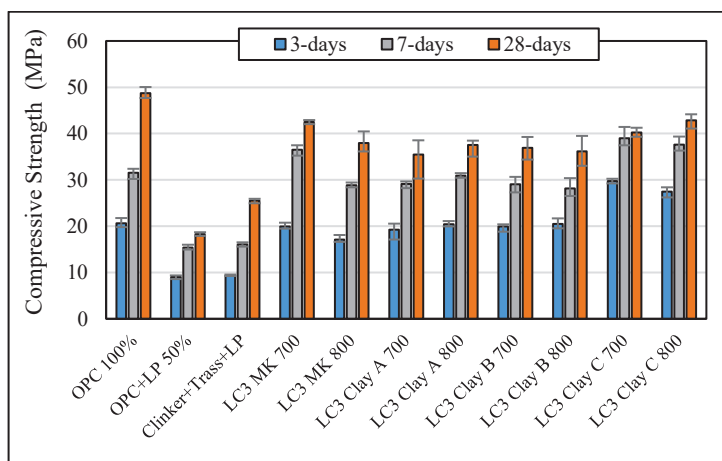


Fig. 3. The compressive strength development of the LC3 mixtures

The OPC+LP 50% was referenced for a 50% OPC substitution with inert material, while Clinker+Trass+LP provided a comparison for substituting calcined clay with trass in LC3 system. The trass samples, comparable to the OPC with 50% filler (OPC+LP 50%) at early ages, showed only a slight strength uptick by day 28. This suggests a pozzolanic reaction, albeit less distinct than LC3 mixtures with metakaolin or calcined clay, and incompatibility of trass in the LC3 system.

Table 5 presents the Strength Activity Index (SAI) of the mixture. The SAI, when compared to OPC, offers critical insights into LC3's performance. A superior SAI suggests it is nearing the strength of the OPC control binder. Considering LC3-50 has a 50% clinker substitution, an SAI beyond 50% implies the utilized calcined clay is reactive, enhancing the LC3 mixture's strength. The OPC+LP 50% sample, serving primarily as filler, further substantiates the reactivity of local clay in LC3, while the

Clinker+Trass+LP acts as a ternary blend comparison. With limestone as the sole inert filler, a 28-day SAI of 37% was observed. However, the Clinker+Trass+LP blend exhibited a modest increase, achieving a 52% SAI. This underscores some strength boost from the pozzolanic reaction, though not as significant as in the LC3 blends. Even with 50% clinker replacement in LC3 samples using local clay, an SAI surpassing 50% was realized. The efficacy of the LC3 ternary blend is prominent, especially in high-kaolinite content samples like LC3 MK and LC3 clay C. These blends—consisting of 50% clinker, 30% calcined clay/metakaolin, 15% limestone, and 5% gypsum—managed an 87% SAI. This indicates that the synergy between calcined clay and limestone can achieve an SAI just 13% shy of the OPC control, despite the 15% limestone inclusion. Still, these strengths were unmatched by the LC3 blends. Each LC3 variant attained an SAI above 70%, with the clay B sample (SAI 74%) nearly reaching the LC3 Metakaolin's strength (SAI 87%). However, relying on clays with excessively high kaolinite content may not be cost-efficient, as it doesn't yield significant strength benefits.

When trass was employed in the LC3 system as a substitute for calcined clay, its early performance was comparable to OPC with a 50% filler. Although trass have shown potential pozzolanic reactions, its strength didn't surpass that of LC3 mixtures using kaolinite clay. While trass serves as a cost-effective alternative, its performance in the LC3 system is context-dependent, often hinging on economic considerations or local material availability.

Table 5. Strength activity index of the investigated mortar compared to the control OPC sample.

No.	Mixture name	Strength Activity Index (%)			No.	Mixture name	Strength Activity Index (%)		
		3-days	7-days	28-days			3-days	7-days	28-days
1	OPC 100%	100	100	100	6	LC3 Clay A 700	93.38	92.26	76.41
2	OPC+LP 50%	43.88	48.72	37.46	7	LC3 Clay A 800	99.07	98.14	77.07
3	Clinker Trass LP	45.52	50.9	52.37	8	LC3 Clay B 700	96.53	92.14	75.76
4	LC3 MK 700	96.51	115.73	87.21	9	LC3 Clay B 800	99.39	89.27	74.15
5	LC3 MK 800	82.9	91.44	77.92	10	LC3 Clay C 700	144.14	123.69	87.93
					11	LC3 Clay C 800	132.91	119.4	82.54

The impact of calcination temperature on the mechanical properties of LC3 samples is evident, particularly in terms of final compressive strength. For LC3 samples with calcined clays A and B, compressive strengths were comparable regardless of whether the calcination temperature was 700°C or 800°C. Conversely, a decrease in strength at 800°C relative to 700°C was observed for both LC3 MK and LC3 Clay C.

Considering Khaled et al.'s study [18], metakaolin begins its recrystallization phase at temperatures above 700°C. Given the high kaolinite content of 85.84% in the MK, the marked reduction in strength between 700°C and 800°C can likely be ascribed to significant metakaolin recrystallization at the higher temperature. Similarly, LC3 Clay C, which contains 49.51% kaolinite displayed a notable strength reduction at 800°C, though the decline was less dramatic than the LC3 MK sample. This behavior highlights the increasing importance of calcination temperature in relation to kaolin content, particularly in the context of strength degradation at elevated temperatures.

Based on the results, calcining clay beyond 700°C doesn't seem beneficial; in fact, it could detrimentally affect the sample's strength. It's crucial to note that the ideal calcination temperature for kaolinitic clay might differ from that of pure kaolin. The optimal temperature for a specific clay can be identified using TGA tests. Factors such as kaolin and other mineral compositions in the clay can influence the TGA curves, which in turn dictate the optimal temperature for that clay. For best results, calcination should proceed at this temperature until a stable Loss on Ignition (LOI) is reached and a consistent color change indicates full calcination.

4 Conclusions

East Java, while not prominently highlighted for its kaolin clay deposits, surprisingly offers a diverse range of kaolinitic clay. A detailed evaluation of this study presents several significant findings:

- **Availability and Kaolin Content:** An analysis of the feasibility of the local clay specimens from East Java underscores their promising kaolin content, with the three samples registering more than 39%. This indicates the widespread availability of kaolinitic clay in various East Java regions. More importantly, the intrinsic performance of these clays, even those with the least kaolinite content, successfully achieved a commendable Strength Activity Index, surpassing 75%.
- **Performance Comparison with LC3 Metakaolin:** The LC3 mixtures, integrated with the local East Java clay, have exhibited strength metrics in close competition with LC3 metakaolin. It's noteworthy that LC3 mixtures developed with local clay having a kaolinite content of 49.51% achieved similar compressive strength of LC3 MK, which contains a higher kaolin content of 85.84%. This not only attests to the binding potential of the local clay but also underscores its suitability as a viable alternative.
- **Optimal Calcination Parameters:** The research findings pinpoint the optimal calcination conditions for the clays in question. A temperature of 700°C sustained for 90 minutes is sufficient to calcinate the kaolin within the clay. This assertion is supported by XRD results, which confirm that over 90% of the kaolin content in the clay underwent calcination under these conditions.
- **Quartz Content and Reactivity:** The presence of quartz, recognized as an inert constituent in the clay, tends to dilute the overall reactivity of the calcined clay within LC3 mixtures. The higher the quartz content, the more muted the reactive capabilities of the clay, presenting avenues for future research and optimizations.

In summation, this study underlines the potential of East Java's local kaolinitic clay in the production of LC3 mixtures. With strategic optimizations and informed decisions on material selection and processing, these local resources can pave the way for sustainable and effective construction solutions.

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References

1. S. J. and L. K.H., *Civil Engineering Dimension* **17**, (2015)
2. A. Manaf and V. Indrawati, *Journal of the Korean Chemical Society* **55**, 490 (2011)
3. B. Lothenbach, K. Scrivener, and R. D. Hooton, *Cem Concr Res* **41**, 1244 (2011)
4. C. He, B. Osbaeck, and E. Makovicky, *Cem Concr Res* **25**, 1691 (1995)

5. A. Tironi, M. A. Trezza, A. N. Scian, and E. F. Irassar, *Cem Concr Compos* **37**, 319 (2013)
6. M. Antoni, J. Rossen, F. Martirena, and K. Scrivener, *Cem Concr Res* **42**, 1579 (2012)
7. R. Kaminskas, D. Monstvilaite, and V. Valanciene, *Advances in Cement Research* **30**, 231 (2018)
8. R. Jaskulski, D. Józwiak-Niedźwiedzka, and Y. Yakymchko, *Materials* **13**, 4734 (2020)
9. K. Scrivener, F. Martirena, S. Bishnoi, and S. Maity, *Cem Concr Res* **114**, 49 (2018)
10. K. Scrivener, F. Avet, H. Maraghechi, F. Zunino, J. Ston, W. Hanpongpun, and A. Favier, *Green Mater* **7**, 3 (2019)
11. K. Ram, M. Flegar, M. Serdar, and K. Scrivener, *Materials* **16**, 374 (2022)
12. M. Sharma, S. Bishnoi, F. Martirena, and K. Scrivener, *Cem Concr Res* **149**, 106564 (2021)
13. P. Lehmann, B. Leshchinsky, S. Gupta, B. B. Mirus, S. Bickel, N. Lu, and D. Or, *Geophys Res Lett* **48**, (2021)
14. S. Joseph, A. M. Joseph, and S. Bishnoi, in (2015), pp. 501–507
15. B. Ayati, D. Newport, H. Wong, and C. Cheeseman, *Cleaner Materials* **5**, 100099 (2022)
16. F. Zunino and K. Scrivener, *Cem Concr Res* **153**, 106693 (2022)
17. O. Canbek, Q. Xu, Y. Mei, N. R. Washburn, and K. E. Kurtis, *Cem Concr Res* **160**, 106925 (2022)
18. Z. Khaled, A. Mohsen, A. Soltan, and M. Kohail, *Ain Shams Engineering Journal* **14**, 102142 (2023)